POWER FIBERS:
THIN-FILM BATTERIES ON FIBER SUBSTRATES

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ABSTRACT: Under a DARPA contract ITN has developed solid-state thin-film rechargeable batteries on fiber substrates for energy and power storage in novel stand-alone thin-film battery applications, power composites, and electrotextiles. The basic solid-state thin-film rechargeable battery technology was first invented at Oak Ridge National Laboratory, TN, USA, in the '90s and since 2000 has been taken to next level by ITN with the invention of PowerFibers, which were first demonstrated in early 2001. The basic concept of PowerFibers is to marry power/energy properties with mechanical properties while making the thin-film batteries become a part of and take over some functions of the load-bearing mechanical structure. This novel design reduces the mass and volume fraction of the parasitic, non-power supplying, strictly mechanical parts in applications where those dimensions are critical. In addition to this basic concept, PowerFibers provide a unique form factor, defined by a large length-to-diameter ratio, which permits small bending radii and substantial flexing. Such mechanical properties are prerequisites for potentially using PowerFibers in novel thin-film battery applications. An advantage of PowerFibers over flat flexible thin-film batteries fabricated on foil substrate is the inherently larger surface area of PowerFibers, which in turn is proportional to the power and energy of a given type of thin-film battery. Thus, for example, a thin-film battery fabricated on a 50 μm thick foil substrate of 1 cm x 1 cm area has a maximum available battery area of 2 cm^2 (double-sided fabrication) compared to 6.28 cm^2 of two layers of 25 μm thick PowerFibers of 1 cm length. At ITN, PowerFibers have been fabricated as a) single, power supplying fibers as alternatives for flat, thin-film batteries and b) power composites containing tens to hundreds of PowerFibers. The PowerFibers in the power composites were cycled electrochemically under ambient conditions for more than 2000 times while losing less than 0.025% capacity per cycle.

KEYWORDS: rechargeable, flexible, thin-film battery, fiber, composite

INTRODUCTION

ITN Energy Systems Incorporated has developed flat, rechargeable thin-film lithium batteries, based on the technology of Oak Ridge National Laboratory, that have been demonstrated at ITN to cycle over 90,000 times at 100% depth of discharge at 0.5 mA/cm^2 between 4.2 and 3.0 V with an average capacity loss of 0.0004% per cycle. This unsurpassed performance in lithium battery technology showed that thin-film batteries can be built which are still be able to deliver more than 60% of their initial capacity after 90,000 cycles.

Encouraged by this outstanding performance ITN Energy Systems has received funding under DARPA's Synthetic Multi-Functional Materials (SMFM) Program since December 2000 to build the first ever rechargeable thin-film batteries around a variety of different fiber substrates, which we termed PowerFibers. The basic concept behind PowerFibers is to marry at least two different functions directly on the fiber level, which are of electrochemical (power and energy storage) and mechanical (structural) nature. As a result, PowerFibers can be utilized as individual reinforcement fibers in (polymeric) composites or as members of smaller and larger networks that form specific architectures. In both cases PowerFibers enable the integration of power and energy into those structures at almost no additional weight or volume so that the resulting novel structural architectures become either one large battery or a multitude of (different) batteries. On the other hand, the thin-film battery layers on the fibers are quite

flexible and mechanically robust thereby contributing as well to the overall mechanical properties of the composites or structural architectures. From this angle one has to view PowerFiber arrays as mushroom-root like power/energy sources with built-in specific architecture or specific architectures with built-in, spread-out power/energy capability. Thus, PowerFibers have created a technologically novel synergy and symbiosis of structure and power/energy. The next higher functionality stage in PowerFiber evolution was the marriage of the two PowerFiber functions on the system level at close proximity (about 1 - 100 μm) with the function(s) of the composite material into which the PowerFibers have been integrated. The evolution from the basic, individual PowerFiber to the so-called PowerComposite is illustrated in Figure 1.
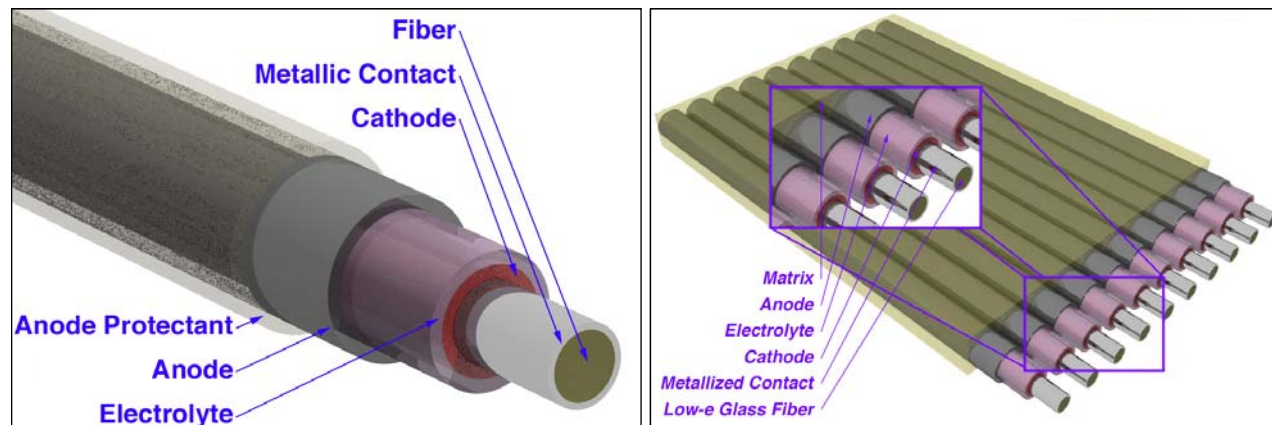

Figure 1: (Left) Invidual PowerFiber (= complete thin-film battery fabricated around a fiber substrate) providing at least two different functions: Power/energy storage and structural/mechanical properties. (Right) PowerComposite (= more than one PowerFiber integrated into a composite structure) providing at least two different, in many cases rather three or more, functions on the system level at close proximity (about 1 – 100 μm) such as power/energy, structural/mechanical properties, and optionally optical and acoustic functions, which are additionally contributed by the matrix material of the composite.

Having demonstrated the feasibility of PowerFibers on a variety of different fiber substrates (Sapphire, SiC, carbon, borosilicate glass, Cu, stainless steel, Inconel, NiTi shape memory alloy, and Ti6-4) with diameters ranging from 33 μm to 150 μm and equipped with thin-film batteries of different configurations (Li-free (3), inverted Li-free (6), Li-ion (4), inverted Li-ion (6), and Li metal (5)), ITN is presently in the process of improving the electrochemical properties of the thin-film battery before re-focusing on the optimization of the mechanical properties of the individual PowerFibers as well as selected PowerComposites. This paper summarizes our achievements in PowerFiber and PowerComposite technology up to the end of CY 2002.

EXPERIMENTAL

ITN Energy Systems has developed a rotational shadow mask system that allows the sequential vacuum deposition of the individual thin-film battery component layers in a selected geometry. For the vacuum depositions, magnetron sputtering and electron-beam evaporation were used. A schematic cross-sectional view perpendicular to the longer axis of a PowerFiber is shown in Figure 2 for which the list of fiber materials used has been given above. In most cases the electrolyte was a lithium phosphorus oxynitride glass of the approximate stoichiometry $Li_{3.1}PO_{3.3}N_{0.5}$, known in the literature as "Lipon", which was invented at Oak Ridge National Laboratory in 1992 (1, 2). Depending on the choice of the positive cathode material (nanocrystalline $Li_{1.6}Mn_{1.8}O_4$, nanocrystalline $Li_2V_2O_5$, or crystalline $LiCoO_2$), the cathode current collector (ccc) was typically Cr, Cu or Au. To demonstrate feasibility we fabricated a

variety of thin-film battery configurations which determined the choice and, in particular, the thickness of the negative anode material. Figure 2 shows the schematic of a non-inverted configuration in which the anode is sitting furthest away from the substrate. All possible non-inverted configurations have been demonstrated experimentally with PowerFibers, such as the "Li metal" configuration (metallic lithium anode (5)), the "Li-ion" configuration (has a lithium ion anode such as SnN_x ($0.5 < x < 1.33$)) (4), and the "Li-free" configuration (equipped with a metallic anode current collector onto which a metallic lithium thin-film is electroplated in-situ during charge of the battery without forming any lithium intermetallic compounds) (3).
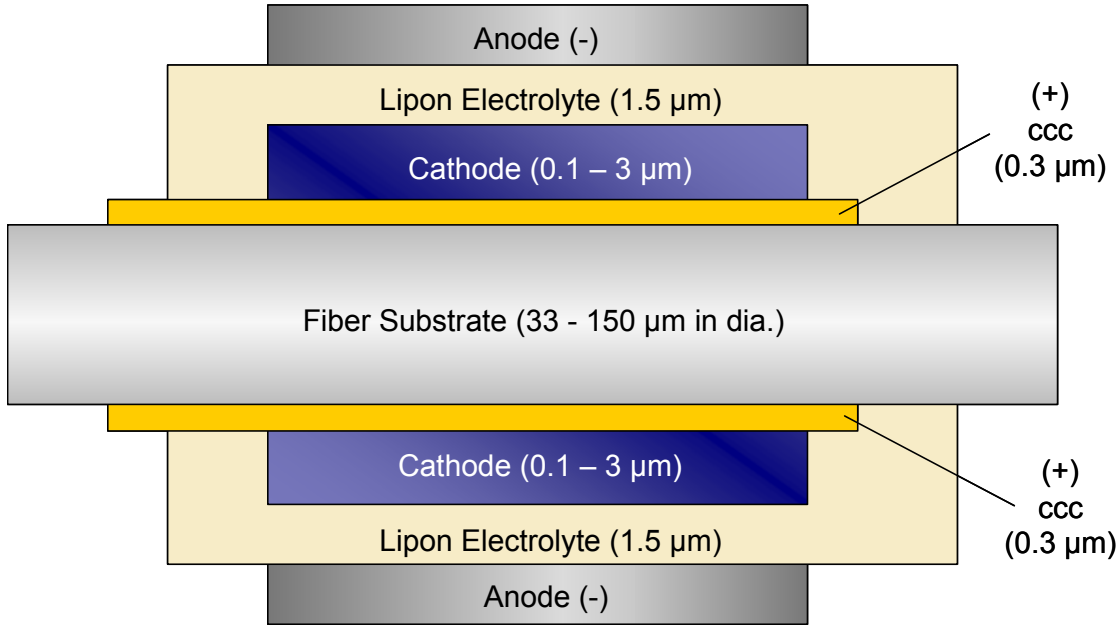

Figure 2: Schematic cross-sectional view perpendicular to the longer axis of a PowerFiber. The given dimensions are typical thicknesses for the individual thin-film battery component layers. For specific material selections refer to text.

In the inverted (or buried) configuration the negative anode is located closest to the substrate and the positive cathode is sitting "outside" of the electrolyte. Except for the inverted Li metal configuration, all other possible inverted (buried) configurations have been demonstrated in PowerFibers. For the "inverted Li-ion" configuration we used SnN_x ($0.5 < x < 1.33$) while for the "Li-free" configuration a Cu or Cr anode current collector was employed. Selected PowerFiber configurations on different substrates are shown in the SEM (scanning electron microscope) micrographs of Figures 3 and 4 while indicating that additional, functional layers, as compared to the simplistic schematic in Figure 2, were needed to make the respective PowerFibers operational. The details and reasons for the choice of those additional layers as well as the particular morphology of each layer go beyond the scope of this paper and will be published elsewhere.
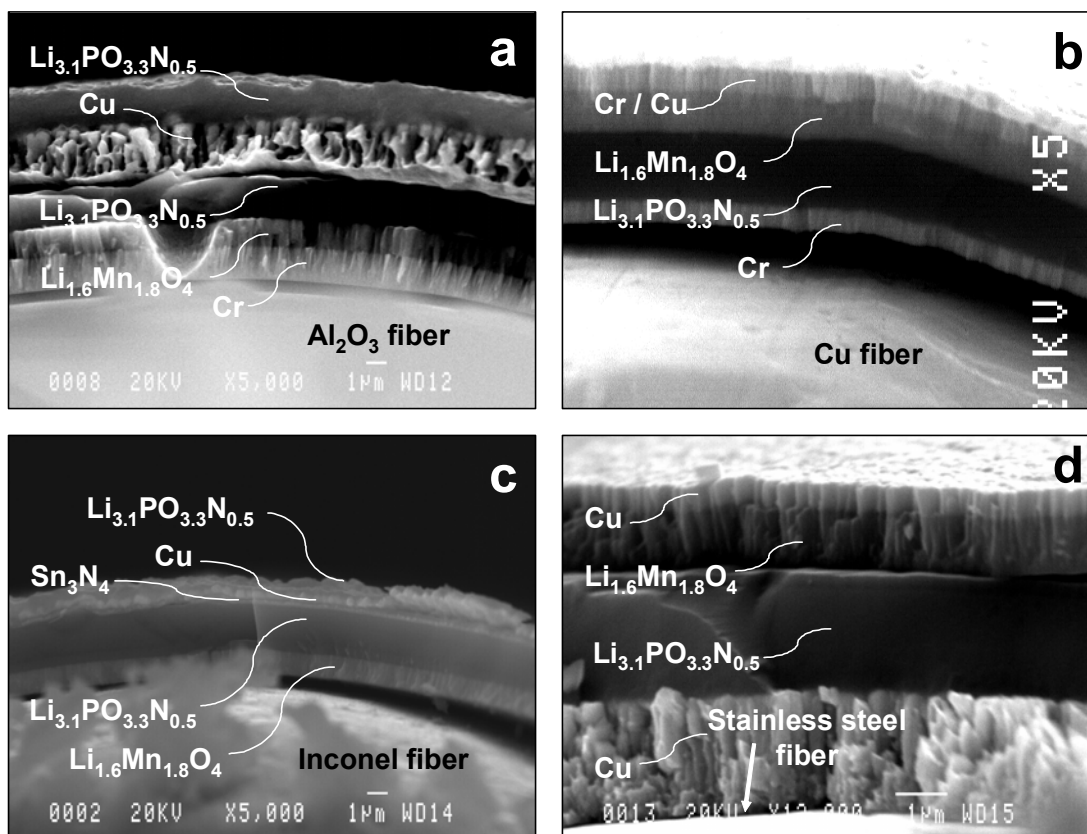
Figure 3: Cross-sectional SEM (scanning electron microscope) micrographs of selected PowerFiber configurations. The micron bars (1 μm) included in the micrographs are provided for scale reference. (a) Non-inverted Li-free PowerFiber configuration on Sapphire (Al_2O_3) fiber substrate with $Li_{3.1}PO_{3.3}N_{0.5}$ ("Lipon") protective overlayer. (b) Inverted Li-free PowerFiber configuration on Cu fiber substrate. (c) Non-inverted Li-ion PowerFiber configuration on Inconel fiber substrate with $Li_{3.1}PO_{3.3}N_{0.5}$ ("Lipon") protective overlayer. (d) Inverted Li-free PowerFiber configuration on stainless steel fiber substrate.

Once the fabrication of the individual PowerFibers was completed, they were tested on their electrochemical and preliminary mechanical properties either as individual, single PowerFibers (see Figure 5) or as PowerComposites. For the PowerComposite integration, as schematically shown in Figure 1 (right) above, we embedded the individual PowerFibers into a 1 mm thick adhesive matrix (3M, Minneapolis, MN) and sandwiched this setup by two PET foils (125 μm thick) that served as a shell for added mechanical functionality and protection. Such a PowerComposite used for demonstration purposes is shown in Figure 6.
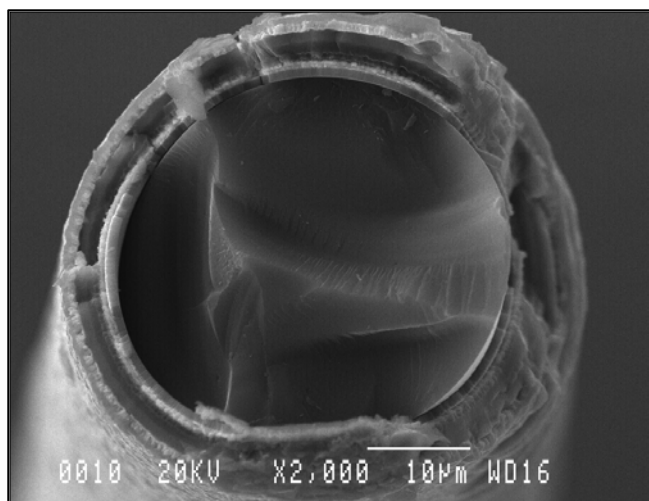
Figure 4: Cross-sectional SEM (scanning electron microscope) micrographs of a PowerFiber fabricated onto 33 µm in diameter carbon fiber substrate. This particular PowerFiber consisted of 8 functional battery layers based on a more advanced chemistry than described above for Figures 2 and 3.

- 150 µm Diameter Sapphire Fiber
- Lithium-Free Battery Configuration
- 1.3 µm a-Li$_{1.6}$Mn$_{1.8}$O$_4$ Cathode (Li source)
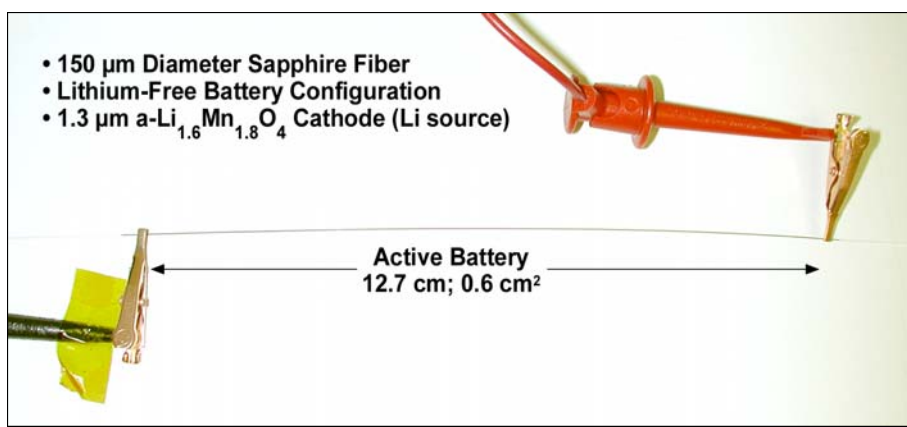
Active Battery
12.7 cm; 0.6 cm²

Figure 5: Electrochemical testing of individual PowerFibers with two alligator clips making electrical contact to the two current collectors that are accessible on opposite sides of the longer PowerFiber axis.

Flexible PET Shell

DARPA/DSO SMFM   PF-A-0ACPL-17-10
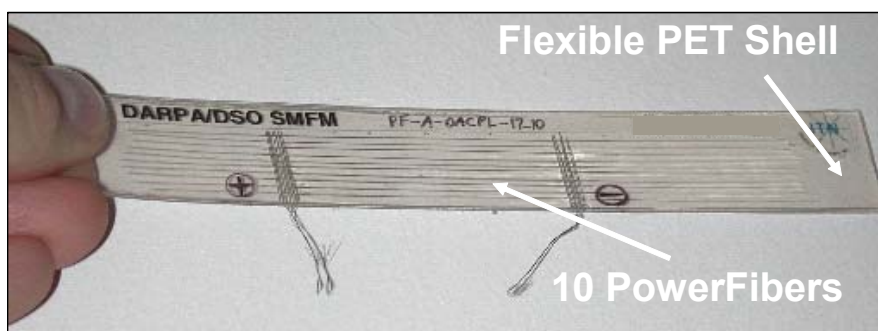
(+)   (-)

10 PowerFibers

Figure 6: PowerComposite consisting of 10 individual PowerFibers that are electrically connected in parallel by auxiliary Cu wires creating a positive (+) and a negative terminal (-). Confer text for details on the PET shell.

RESULTS AND DISCUSSION

Early PowerFiber configurations (time frame CY2001/2002) involved mostly the use of the nano-crystalline cathodes Li$_{1.6}$Mn$_{1.8}$O$_4$ and Li$_2$V$_2$O$_5$, which both are known to exhibit an inherently limited energy and power capability, in particular at moderate (0.1 mA/cm^2) to higher (>1 mA/cm^2) current rates. However, the fabrication of these cathodes could be accomplished in the as-deposited state without any further high-temperature, post-deposition treatments. For this reason both cathode materials were

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considered suitable materials to study and demonstrate the feasibility of a variety of different PowerFiber configurations. Employing the nano-crystalline $Li_2V_2O_5$ in an inverted Li-free configuration together with a Cu anode current collector we proved that such PowerFibers embedded in a PowerComposite (8 PowerFibers electrically connected in parallel) can be cycled for more than 2000 cycles at 100% depth of discharge at a ~50 C discharge rate (50 times higher than commercial rechargeable batteries) while being able to deliver still more than 50% of their initial capacity during each discharge cycle after 2000 cycles (cf. Figure 7 (left)). From these values one calculates an average capacity loss of only 0.025% per cycle, which is about 4-10 times lower than typical commercial rechargeable lithium-ion and polymer batteries. The same figure also confirms that in each cycle the discharge and charge capacity ratio or coulombic efficiency remains virtually unchanged and close to 100% throughout the 2000 cycles thereby demonstrating no significant leakage development in all of the parallel connected Power Fiber batteries. A different presentation of the high reversible cycle stability is given by Figure 7 (right), which illustrates the discharge voltage profile as a function of discharge capacity for cycle 10 and cycle 1000. As evident, the discharge voltage profiles barely change over the course of 990 cycles thus corroborating the stable, excellently reversible chemistry of the PowerFiber batteries.
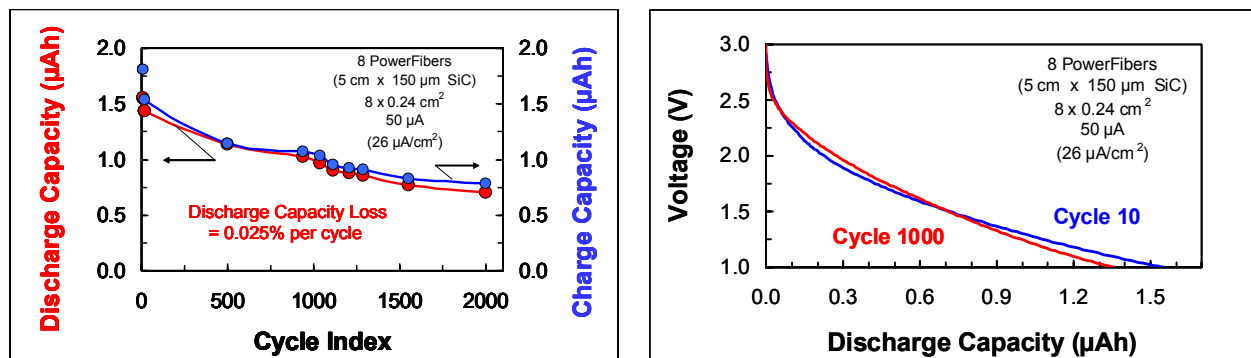

Figure 7: (Left) Discharge and charge capacity as a function of cycle index (or cycle number) of a PowerComposite that consists of 8 PowerFibers. Each PowerFiber was fabricated on a (150 µm in dia.) SiC fiber substrate carrying a 5 cm long and 0.24 cm^2 large active battery area (equal to cathode dimensions). The discharge current through the 8 in parallel connected PowerFibers was 50 µA which amounts to a current rate (or density) of 26 µA/cm^2 or about 50 C. (Right) Discharge voltage profiles as a function of discharge capacity for cycle 10 and 1000.

Instead of using the inferior cathode chemistry of nano-crystalline $Li_2V_2O_5$, ITN Energy Systems has built flat thin-film batteries with crystalline $LiCoO_2$ cathodes and demonstrated more than 90,000 cycles at 100% depth of discharge at a discharge rate of 0.5 mA/cm^2 (8 C rate) between 4.2 and 3.0 V. The integral, irreversible discharge capacity loss over the entire 90,000 came to 38%, which translated into an averaged, extremely low capacity loss of 0.0004% per cycle. The high cycle number of these outstanding rechargeable batteries (~7 µm thick and 1 cm^2 in area) yielded an unprecedented volumetric lifetime capacity and energy for rechargeable batteries of 7700 Ah/cm^3 of and 29.3 kWh/cm^3, respectively, which in terms of absolute lifetime capacity and energy (5.2 Ah and 20.5 Wh, respectively) is about 400% of that of a non-rechargeable D size battery (5.8 cm high and 3.3 cm in diameter) that is commonly used in flash lights. Based on these accomplishments in flat geometry, we are confident that it is possible to achieve such outstanding performance in round thin-film batteries (PowerFibers) as well.

Recently, we obtained the first electrochemical performance results of PowerFibers based on the crystalline $LiCoO_2$ cathode chemistry in Li-free (anode) configuration. By comparison with $LiCoO_2$ voltage profiles from the literature (5) it becomes evident that the voltage profile of our $LiCoO_2$ batteries on PowerFiber exhibit the characteristic shape of a long plateau at about 3.9 V with two minor plateaus at

about 4.06 V and 4.16 V (cf. Figure 8). The capacity obtained in the electrochemical experiment shown in Figure 8 is equal to the theoretical capacity of $LiCoO_2$ charged to 4.2 V and amounts to about 70 µAh per 1 cm^2 and 1 µm of $LiCoO_2$ volume.
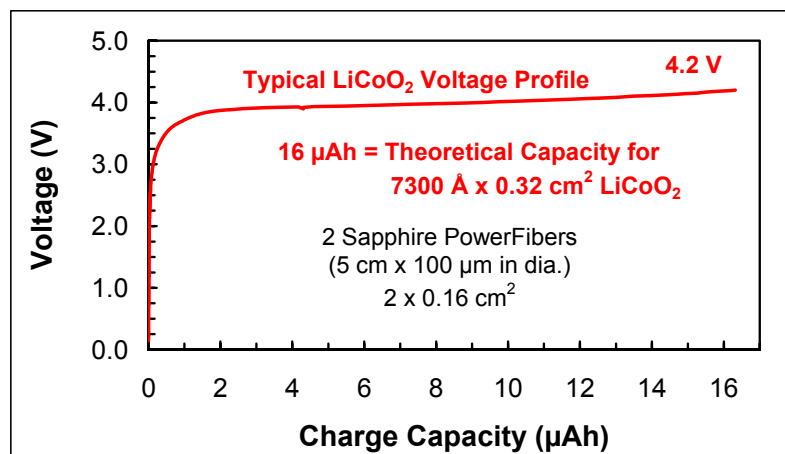

Figure 8: PowerComposite consisting of two PowerFibers (100 µm in dia. Sapphire fiber substrate) with crystalline $LiCoO_2$ cathodes each having an active length of 5 cm and an active area of 0.16 cm^2, which doubled (0.32 cm^2) due to the electrical parallel connection of both PowerFibers. The PowerFiber configuration was Li-free with a Cu anode current collector.

With a different PowerComposite containing five $LiCoO_2$ based PowerFibers, which were fabricated on 100 µm in dia. Sapphire fiber substrates with a 5 cm long active battery area each, we broke the unofficial "sound barrier" for lithium based batteries by exceeding a current rate of 1 mA/cm^2 (Figure 9). Although the discharge energy under these more extreme conditions was delivered between 3.0 and 0 V with a midpoint voltage of about 1.5 V, instead of about 3.7 V as we achieve regularly in our flat thin-film batteries, this performance was an important milestone in our PowerFiber technology. The result on the 0.5 mA (0.63 mA/cm^2) discharge profile (cf. Figure 9) with a midpoint voltage of about 3.2 V holds great promise that soon the performance of PowerFibers will be comparable to that of our flat thin-film batteries, which can presently be operated at up to 30 mA/cm^2 between 4.2 and 2.0 V and at 25°C.
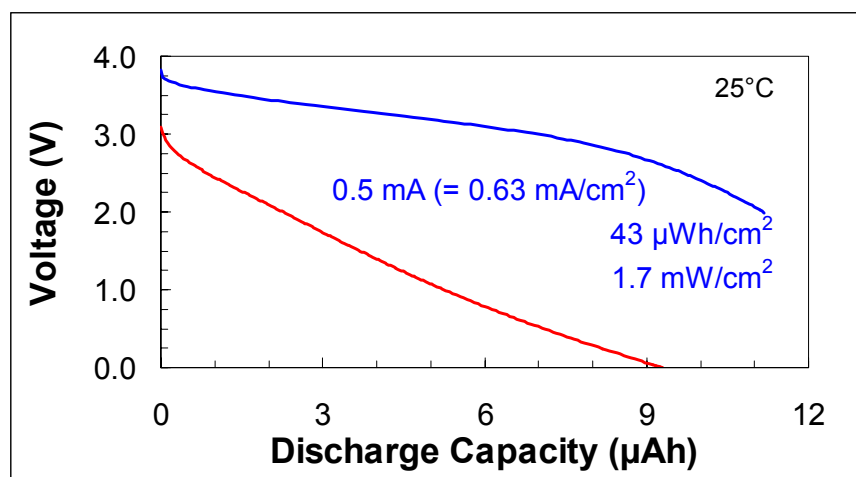

Figure 9: PowerComposite consisting of five parallel connected PowerFibers (100 µm in dia. Sapphire fiber substrate) with an integral, active battery area of 0.8 cm^2 over 5 cm length. The PowerFiber configuration was Li-free with a Cu anode current collector. These preliminary results show that such a PowerComposite can deliver power of 1.4 mW / 0.8 cm^2 = 1.7 mW/cm^2.

A potential advantage of PowerFibers over flat, flexible thin-film batteries fabricated on foil substrate is the inherently larger surface area of PowerFibers, which in turn is proportional to the power and energy of a given type of thin-film battery. This idea is schematic illustrated in Figure 10. It becomes evident from

that figure, the maximum area of thin-film batteries fabricated on a 50 μm thick x 1 cm^2 flat substrate is 2 cm^2 (double-sided fabrication) compared to 6.28 cm^2 of two layers of 25 μm thick PowerFibers of 1 cm length. Even if only one layer of 50 μm thick PowerFiber was used, the gain in active battery area would still amount to 57%. Due to the present challenge to fabricate PowerFiber onto fiber substrates much smaller that 50 μm in diameter, it remains to be seen whether or not this PowerFiber approach introduces a commercially viable alternative to the flat thin-film battery on foil substrate.
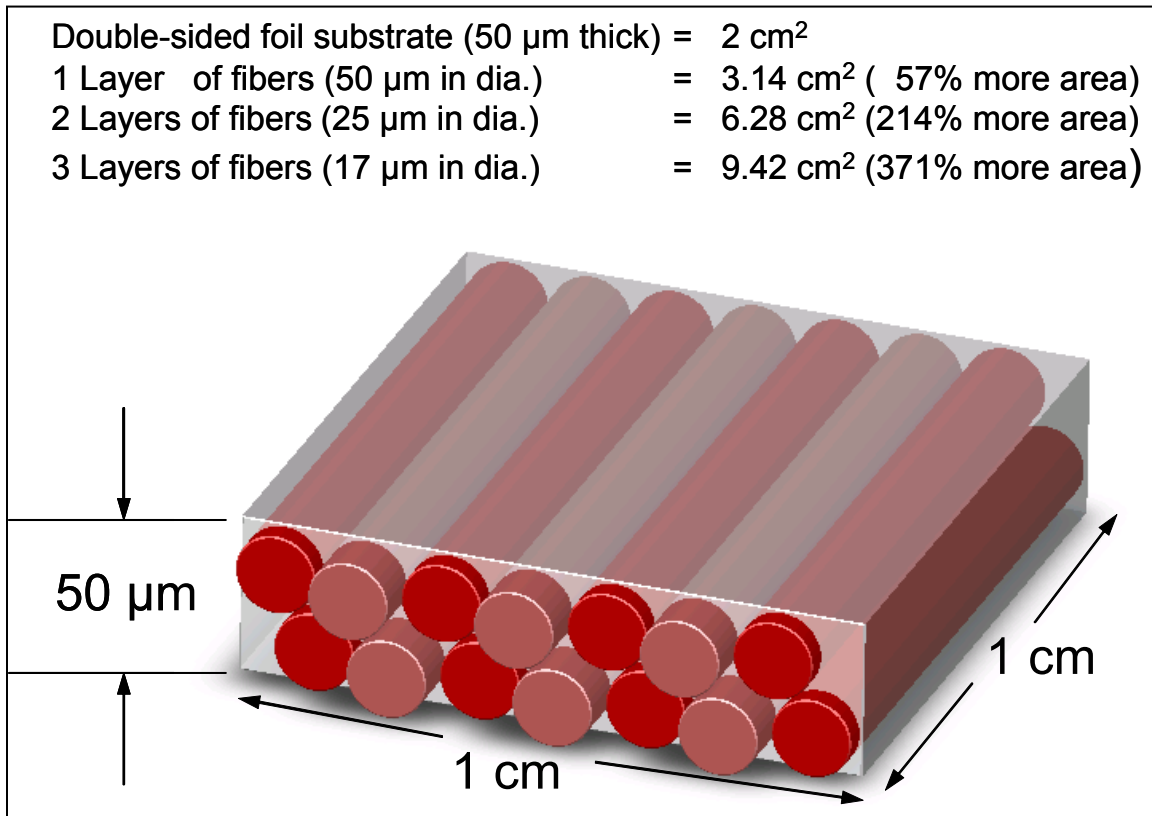

Figure 11: Comparison between the useable battery area of a flat 50 μm thick foil substrate (commonly used by ITN for the fabrication of flat thin-film batteries) and a PowerFiber array of the same footprint and overall volume. Note that thin-film batteries can practically not be fabricated on the edge of such a foil substrate so that only both face sheet surfaces (2x 1 cm^2 = 2 cm^2) are available.

SUMMARY AND CONCLUSIONS

We demonstrated the successful fabrication and operation of a variety of thin-film battery configurations around fiber substrate. We named these novel, multi-functional thin-film batteries PowerFibers, in which at least one mechanical function is married with the electrochemical function directly on the fiber level. That is, the mechanical properties of the individual battery component layers add to the mechanical features of the fiber substrate. PowerFibers may either be used as individual power/energy sources with unique mechanical properties and form factor or combined inside a matrix to form the next higher level of functionality, the so-called PowerComposites. The matrix in PowerComposites usually contributes additional mechanical, optical, acoustic, electrical, or magnetic properties/functions to its PowerFiber core thus increasing the order of multi-functionality in the PowerComposite.

PowerFibers and PowerComposites hold great promise for unique future power/energy sources. Having previously demonstrated the same $LiCoO_2$ based battery chemistry in flat thin-film batteries for more than 90,000 cycles at 100% depth of discharge with an extremely low capacity loss of 0.0004% per electrochemical cycle, we anticipate that soon PowerFibers and PowerComposites will become comparably powerful to their flat counterparts and then replace them in specific commercial and military applications. For instance, 10 cm x 10 cm patches consisting of 1000 PowerFibers are projected to deliver 9 W at 3 V and 3 A while supplying 0.1 Wh of energy. This anticipated trend may be further leveraged by the inherently higher active battery area of PowerFibers compared to the state-of-the-art flat thin-film batteries, which are fabricated on 50 μm thick foil substrates. However, to take full advantage of this option, PowerFibers would need to be fabricated on fiber diameters on the order of 25 μm or even smaller. Work is in progress at ITN Energy Systems that is addressing this issue.

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